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(71) Applicant: MITSUBISHI MATERIALS CORPORATION
6-1, Otemachi 1-chome
Chiyoda-ku Tokyo(JP)

(72) Inventor: Ogi, Katsumi Mitsubishi Materiaru K.K.
Chou-Kenkyusho-nai 1-297 Kitabukuro-cho
Omiya-shi Saitama-ken(JP)
Inventor: Soyama, Nobuyui Mitsubishi Materiaru K.K.
Chuo-Kenkyusho-nai 1-297 Kitabukuro-cho
Omiya-shi Saitama-ken(JP)
Inventor: Mieda,Akihiko, Mitsubishi Materiaru K.K.
Chuo-Kenkyusho-nai 1-297 Kitabukuro-cho
Omiya-shi Saitama-ken(JP)

(74) Representative: Strehl, Schübel-Hopf, Groening
Maximilianstrasse 54 Postfach 22 14 55
W-8000 München 22(DE)

(54) Method for controlling crystal orientation of ferroelectric thin film.

(57) In the production of ferroelectric PZT of PLZT thin film by the sol-gel method, application of precursor solution (sol) onto a substrate is followed by heat-treatment for pyrolysis at 150 - 250 °C, 250 - 359 °C, or 450 - 550 °C, and further firing for crystallization at 500 - 800 °C, whereby crystal orientation in the direction of the (111) plane, or the (111) and (100) planes, or the (100) and (200) planes can be effected.

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Filed of the invention

The present invention relates to a method for controlling the crystal orientation of ferroelectric thin film of lead zirconate titanate (PZT) or lanthanum-containing lead zirconate titanate (PLZT). PZT thin film or PLZT thin film is used as infrared sensor, piezoelectric filter, vibrator, laser modulating element, optical shutter, capacitor film, non-volatile memory, etc. It has outstanding physical properties with which it can be formed in a sharp, fine pattern on a substrate.

Background of the invention

There are known three methods for forming ferroelectric PZT or PLZT thin film on a substrate. (a) The first one comprises application of a paste of powdery compoud oxide onto a substrate, followed by drying and baking. (b) The second one sputtering. (c) The third one is the so-called sol-gel method which consists of application of a compound precursor compound (such as metal alkoxide in the form of sol) onto a substrate and subsequent heat treatment to bring about crystallization.

Usefulness of ferroelectric thin film is derived from its polarization reversibility. However, polarization reversibility causes crystal strains, which result in fatigue of film. A conceivable countermeasure against crystal strains is to form the thin film in such a way as to grow a single crystal or to orient crystals in the direction of polarization axis. Although there are a lot of reports about the crystal orientation in thin film, most of them are about PZT thin film formed by sputtering and there are few reports about crystal orientation involved in the formation of thin film by the sol-gel method. The sol-gel method is now attracting attention because of its ability to yield good thin film at low temperatures easily and economically.

It is well known that the crystal orientation in the thin film formed by the sol-gel method depends on and usually coincides with the crystal axis of the substrate. However, there is instances where the direction of crystal orientation differs from the crystal axis of the substrate. This makes it difficult to reliably control the crystal orientation of the thin film.

Summary of the invention

The present inventors found that PZT thin film or PLZT thin film formed by the sol-gel method differs in its crystal orientation depending on the temperature of heating of the starting material (precursor) solution (sol) applied onto the substrate. This finding led to the present invention. Accordingly, it is an object of the present invention to provide a method for reliably control the crystal orientation of PZT thin film or PLZT thin film by adjusting the temperature of heat treatment for the precursor solution applied onto the substrate.

To be more specific, it is an object of the present invention to provide a method for controlling the crystal orientation of ferroelectric thin film in which a ferroelectric thin film is formed by application of a precursor solution of lead zirconate titanate or lanthanum-containing lead zirconate titanate onto a platinum substrate with its crystal orientation in the direction of the (111) axis and heating, wherein the precursor solution applied onto the substrate is heat-treated at a temperature in the range of 150 - 550 °C for pyrolysis in accordance with the desired crystal orientation and subsequently at 550 - 880 °C for firing for crystallization, thereby preferential crystal orientation of the thin film is caused in the direction of the specific axis which is determined by the heat treatment temperature.

It is another object of the present invention to provide a method for controlling the crystal orientation of ferroelectric thin film, wherein the application of precursor solution onto the substrate is followed by heat treatment at 150 - 250 °C for pyrolysis and subsequently by firing which causes the thin film to crystallize, with preferential crystal orientation in the (111) plane.

It is sstill another object of the present invention to provide a method for controlling the crystal orientation of ferroelectric thin film, wherein the application of a precursor solution onto the substrate is followed by heat treatment at 250 - 350 °C for pyrolysis and subsequent firing which causes the thin film to crystallize, with preferential crystal orientation in the direction of the (111) plane and (100) plane.

The starting materials used in the present invention are organic acid salts, alkoxides, β-diketone complexes, etc., which are well known in this technical field. They can be used equivalently.

Brief description of the drawings

Figs. 1 to 4 are X-ray diffraction patterns obtained with PZT thin films and the PLZT thin films in accordance with the present invention.

Detailed description of the invention

According to the present invention, PZT thin film or PLZT thin film is formed on a platinum substrate with its crystal orientation in the [111] axis. The substrate should be electrically conductive so that it can be used as the bottom side electrode; in addition, it should not react with PZT thin film or PLZT thin film. Because of these requirements, platinum is a very desirable material. The platinum substrate may be in the form of plate or thin film formed on another substrate. Incidentally, a platinum film formed on a thermally oxidized silicon wafer is oriented in the [111] axis.

The method of the present invention consists of applying a precursor solution of PZT thin film or PLZT thin film, which is a sol of compound organometallic compound as a precursor, onto a platinum substrate oriented in the [111] direction, heat-treating the thus formed film at 150 - 550 °C for pyrolysis, and subsequently firing at 600 - 800 °C for crystallization. The temperature for the first heat treatment (prior to crystallization) should be properly adjusted within a range of from 150 °C to 550 °C so as to control the crystal orientation of the PZT thin film or PLZT thin film.

To be more specific, with a heat treatment temperature adjusted within a range of from 150 °C to 259 °C, it is possible to obtain a PZT thin film or PLZT thin film composed of crystals of perovskite structure preferentially oriented in the (111) plane. Heat treatment at below 150 °C is insufficient for the heat treatment. Heat treatment at above 250 °C causes orientation in the (100) plane in preference to the (111) plane.

With the heat treatment temperature adjusted within a range of from 250 °C to 350 °C, it is possible to obtain a PZT thin film or PLZT thin film composed of crystals of perovskite structure preferentially oriented in the (111) plane and (100) plane. Heat treatment at below 250 °C causes orientation in the (111) plane preferentially. Heat treatment at from above 350 °C up to 450 °C does not cause preferential orientation in the (111) plane and (100) plane.

At the heat treatment temperature adjusted within a range of from 450 °C to 550 °C, it is possible to obtain a PZT thin film or PLZT thin film composed of crystals preferentially oriented in the (100) plane and (200) plane. Heat treatment at below 450 °C causes preferential orientation in the crystal planes other than the (111) plane. Heat treatment at above 550 °C causes premature crystallization.

The firing for crystallization should be carried out within a range of from 550 °C to 800 °C. Heat treatment at above 800 °C causes PZT thin film to react with platinum, resulting in deteriorated physical properties.

The following table shows the relation between the heat treatment temperature and the crystal plane in which crystals orient preferentially.

Heat treatment temperature	Preferential orientation
150 - 250 °C	(111)
250 - 250 °C	(111) and (100)
450 - 550 °C	(100) and (200)

Example 1

In 55g of ethoxyethanol, 7.59g $Pb(CH_3COO)_2 \cdot 3H_2O$, 3.99g $Zr(OBu)_4$ and 2.73g $Ti(OrPr)_4$ were dissolved. The thus obtained precursor solution (sol) was applied to platinum plates, the crystals of which oriented in the (111) axis by means of a spin coater. The coated plates were heat-treated at 200 °C, 300 °C, 400°C, and 500 °C for 15 minutes respectively. The heat treatment was followed by firing for crystallization at 600 °C for 1 hour. Thus there were obtained four samples of PZT ($PbZr_{0.52}Ti_{0.48}O_3$) thin film. They gave X-ray diffraction patterns as shown in Fig. 1 (A: 200 °C. B: 300 °C, C: 400 °C, D: 500 °C). Fig. 1A indicates that the PZT thin film has preferential crystal orientation in the (111) plane. Fig. 1B indicates that the PZT thin film has preferential crystal orientation in the (111) plane and (100) plane. Fig. 1C indicates that the PZT thin film has no preferential crystal orientation in particular planes. Fig. 1D indicates that the PZT thin film has preferential crystal orientation in the (100) plane and (200) plane. With respect to the result shown in Fig. 1A, it is considered that a longer firing will bring about prefential orientation in the (111) axis.

Example 2

The same procedure as in Example 1 was repeated except that the heat treatment was carried out for 1 hour. The resulting samples of PZT thin film gave X-ray diffraction patterns as shown in Fig. 2 (A: 200 °C, B: 300 °C, C: 400 °C, D: 500 °C). This result is similar to that in Example 1.

Example 3

The same procedure as in Example 2 was repeated except that the precursor solution was reflexed for 10 hours before use. The resulting samples of PZT thin film gave X-ray diffraction patterns as shown in Fig. 3.

Example 4

The procedures of Example 1 were repeated using 7.2g of $Pb(CH_3COO)_2 \cdot 3H_2O$, 0.34g of $La(CH_3COO)_3 \cdot 1.5H_2O$, 3.94g of $Zr(OBu)_4$, 2.70g of Ti(OiPr) and 55g 2-ethoxyethanol. The resulting PLZT was $Pb_{0.95}La_{0.05}Zr_{0.51}Ti_{0.47}O_3$. The X-ray diffraction patterns are shown in Fig. 4 (A: 200 °C, B: 300 °C, C: 400 °C and D: 500 °C). Generally, they show characters similar to Fig. 1-3, but preferentiality is improved.

Claims

1. In the method for forming ferroelectric thin film in which a ferroelectric thin film is formed by applying a compound organic metal compound precursor solution (sol) of lead zirconate onto a platinum substrate with crystal orientation in the direction of the [111] axis and heating, an improvement comprising heat-treating said precursor solution (sol) applied onto the substrate at a temperature in the range of 150 - 550 °C for pyrolysis in accordance with the desired crystal orientation and subsequently heating at 550 - 800 °C for firing that brings about crystallization, thereby causing the crystals of the thin film to orient preferentially in the direction of a specific axis.

2. The method for forming ferroelectric thin film as defined in Claim 1, wherein application of said precursor solution (sol) onto the substrate is followed by heat-treatment at 150 - 250 °C for pyrolysis and subsequentl firing which causes the thin film to crystallize with preferential crystal orientation in the direction the (111) plane.

3. The method for forming ferroelectric thin film as defined in Claim 1, wherein application of said precursor solution onto the substrate is followed by heat-treatment at 250 - 350 °C for pyrolysis and subsequent firing which causes the thin film to crystallize, with preferential crystal orientation in the direction of the (111) plane and (1000) plane.

4. The method for forming ferroelectric thin film as defined in Claim 1, wherein application of a said precursor solution (sol) onto the substrate is followed by heat-treatment at 450 - 550 °C for pyrolysis and subsequently by firing which causes the thin film to crystalize, with preferential crystal orientation the in the direction of the (100) plane and (200) plane.

FIG. 1

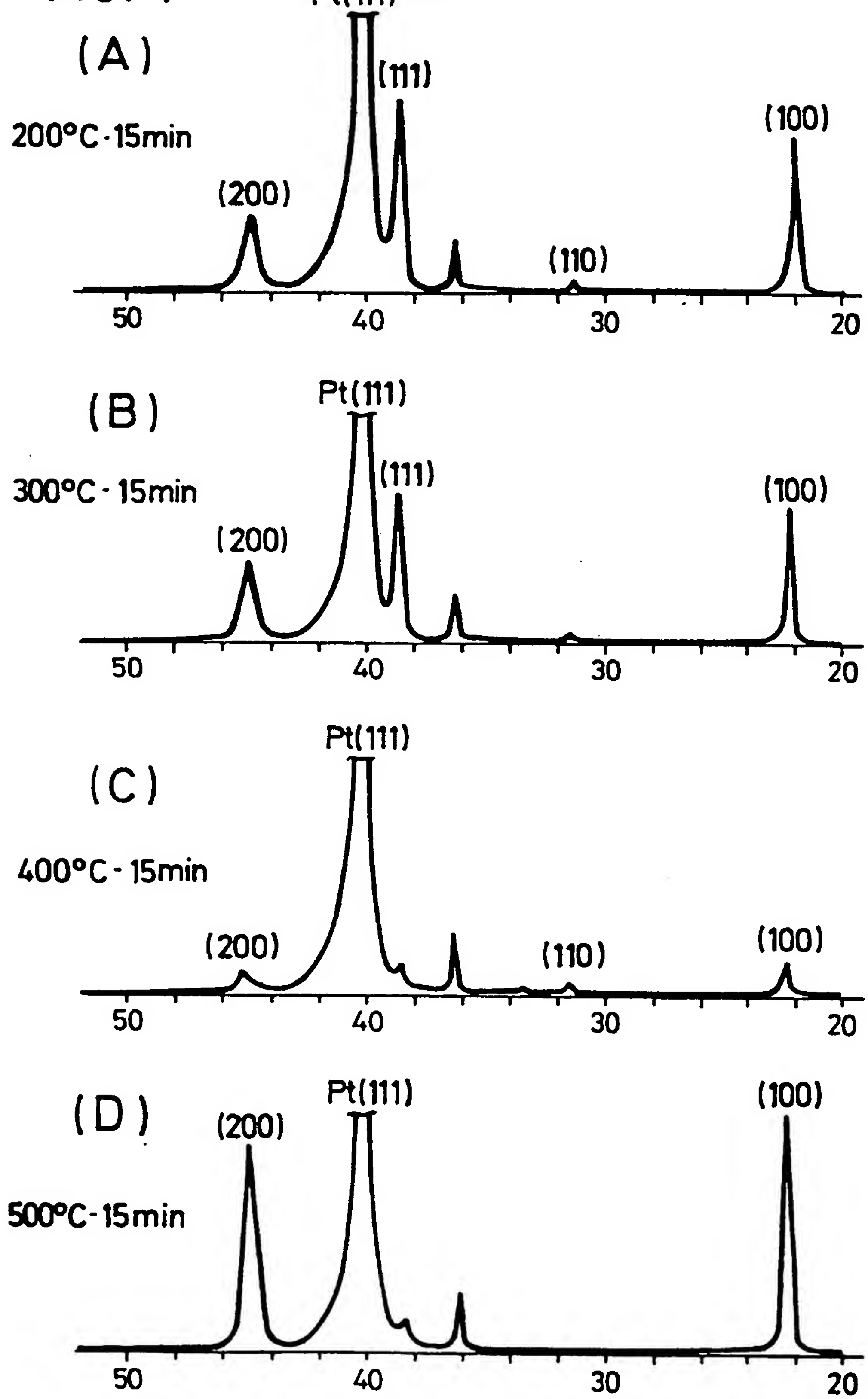
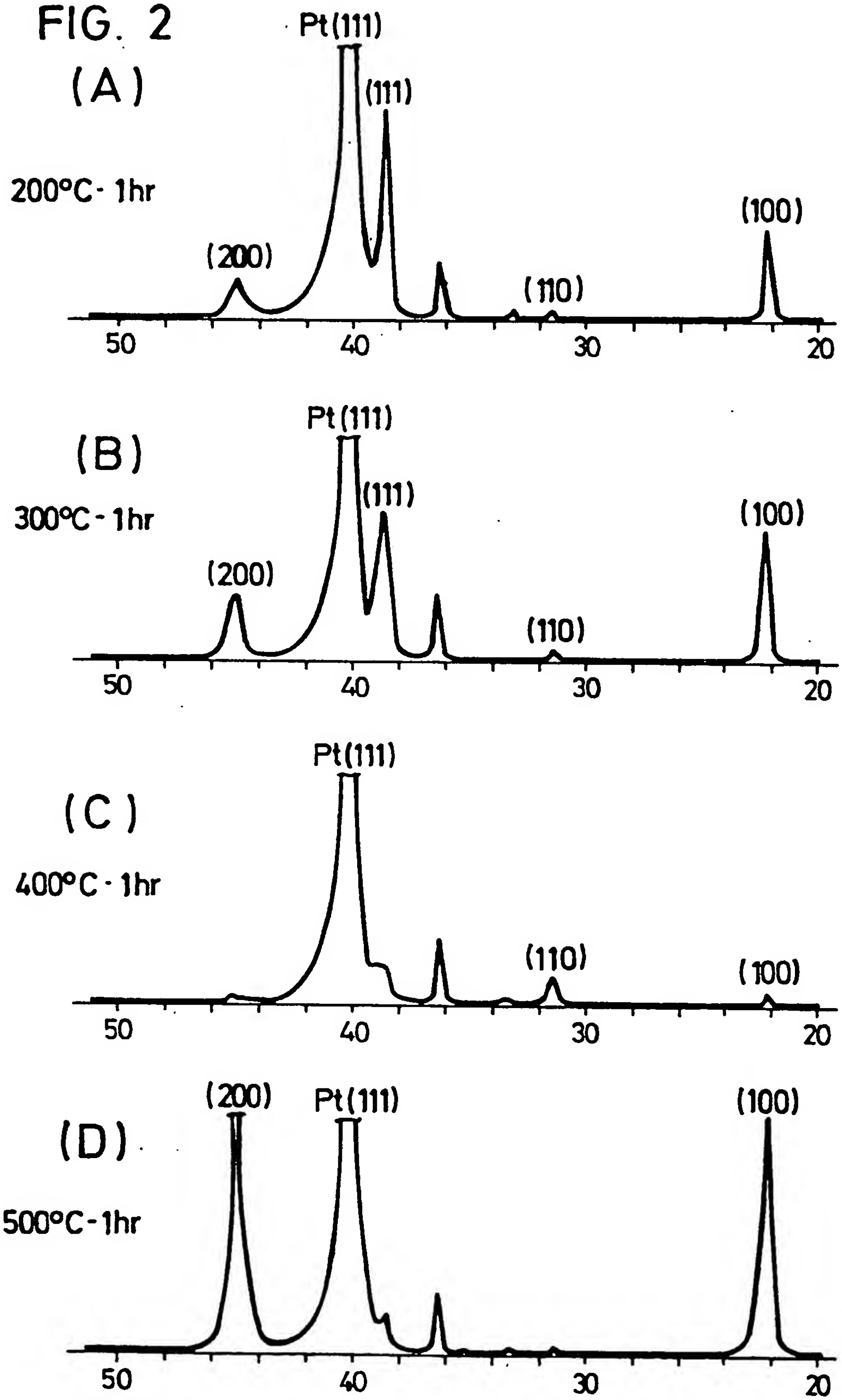

(A)
200°C·15min
Pt(111)
(111)
(200)
(110)
(100)
50
40
30
20
(B)
300°C·15min
Pt(111)
(111)
(200)
(100)
50
40
30
20
(C)
400°C·15min
Pt(111)
(200)
(110)
(100)
50
40
30
20
(D)
500°C·15min
(200)
Pt(111)
(100)
50
40
30
20

FIG. 2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Pt(111)
(111)
(200)
(110)
(100)
50
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Pt(111)
(111)
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40
30
20
(C)
400°C - 1hr
Pt(111)
(110)
(100)
50
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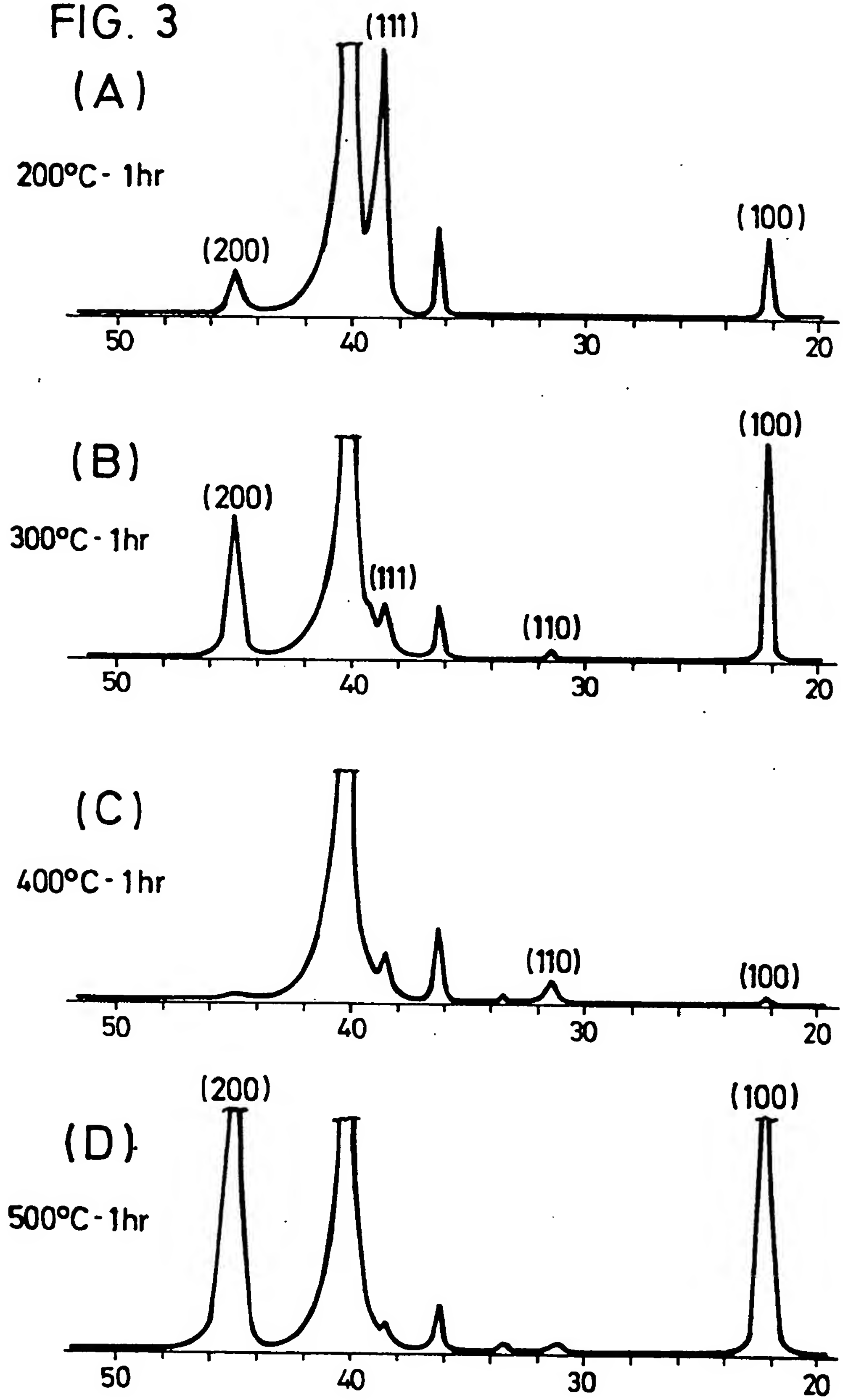
(D)
500°C - 1hr
(200)
Pt(111)
(100)
50
40
30
20

FIG. 3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(100)
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(C)
400°C - 1hr
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(D)
500°C - 1hr
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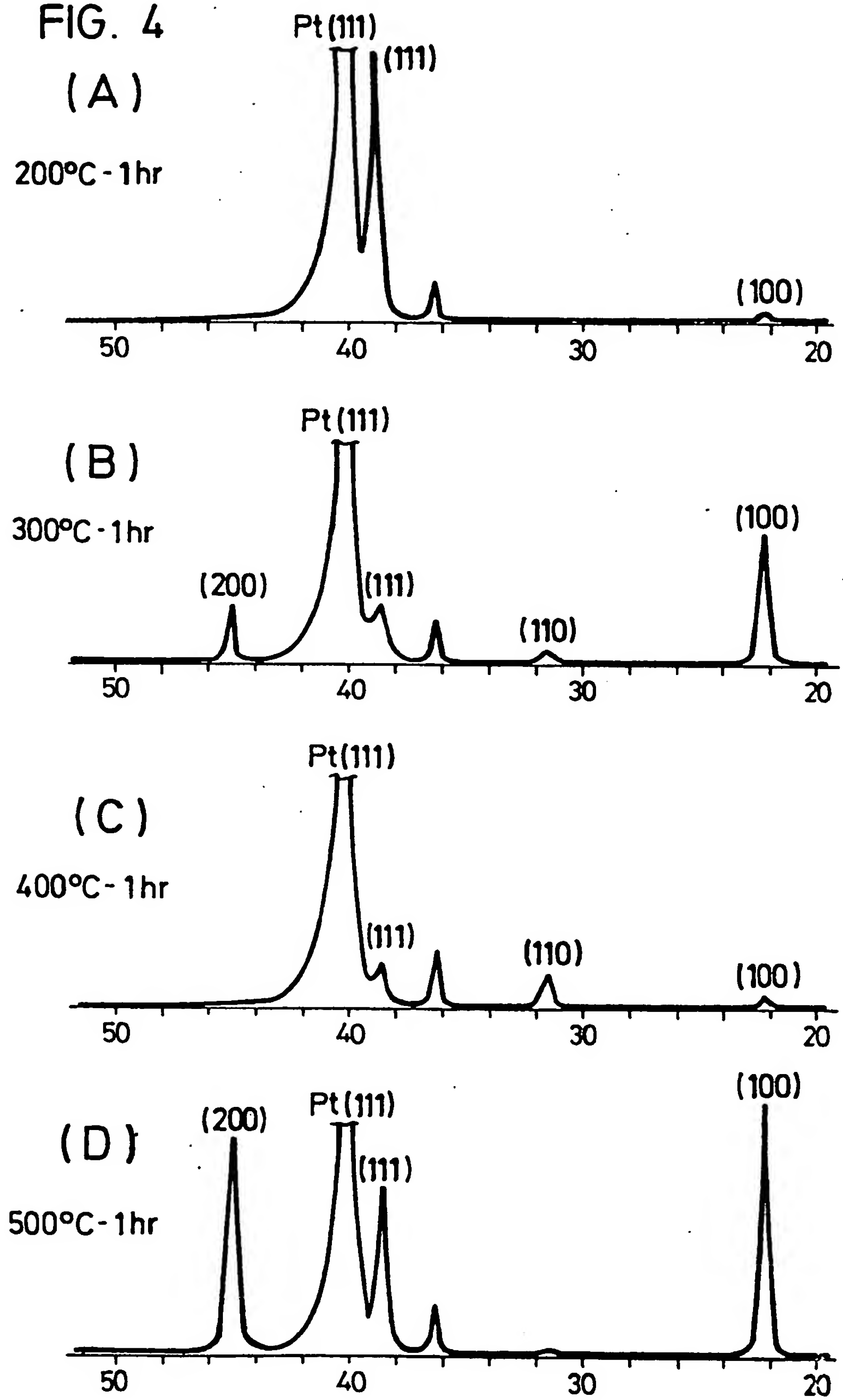
FIG. 4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300°C - 1hr
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(C)
400°C - 1hr
Pt(111)
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(D)
500°C - 1hr
(200)
Pt(111)
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